



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09B 67/22, 63/00	A1	(11) International Publication Number: WO 98/56859 (43) International Publication Date: 17 December 1998 (17.12.98)
(21) International Application Number: PCT/EP97/02991 (22) International Filing Date: 9 June 1997 (09.06.97) (71) Applicant: CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH). (72) Inventors: JAFFE, Edward, Ephraim; 6 Penny Lane Court, Wilmington, DE 19803 (US). DELANEY, James, Martin; 17 Ocheltree Drive, Wilmington, DE 19808 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: COLORANT BLENDS CONTAINING A SALT-FORMING AZO PIGMENT AND A 1,4-DIKETO-3, 6-DI-ARYLPYRROLO(3,4-C)PYROLLE (57) Abstract <p>The present invention relates to colorant blends comprising (a) an azo component, which is a salt of a salt-forming azo pigment of formula (I): A-N=N-B, wherein A is the residue of a diazo component and B is the residue of a coupling component; and (b) a second component, which is an opaque 1,4-diketo-3, 6-diaryl-pyrrolo[3,4-c]-pyrrole pigment. The colorant blends are especially useful in coating compositions such as paints.</p>		

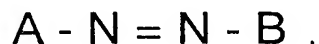
FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

COLORANT BLENDS CONTAINING A SALT-FORMING AZO PIGMENT AND A 1,4-DIKETO-3, 6-DI-ARYLPYRROLO(3,4-C)PYRROLE

The present invention relates to colorant blends comprising (a) an azo component, which is a salt of a salt-forming azo pigment of the formula



wherein A is the residue of a diazo component and B is the residue of a coupling component; and (b) a second component, which is an opaque 1,4-diketo-3,6-diarylpyrrolo[3,4-c]pyrrole (DPP) pigment.

Pigments that are suitable for use as the azo component are well-known in the pigment art and are described, for example, in the Colour Index, International, Third Edition (1971), including the Fourth Revision (1992), which is published by the Society of Dyers and Colorists.

In particular, suitable azo components are salts of the pigments typically prepared by a reaction sequence of diazotization and coupling wherein a diazotizable aromatic amine, which is referred to as the diazo component, is combined with a coupling component, which is typically an activated aromatic compound or a compound containing an activated methylene group. The diazo coupling reaction is well-known to the organic chemist and is described in Willy Herbst et al, Industrial Organic Pigments, VCH (1994) pages 189-343, along with suitable diazo and coupling components and important pigments suitable for use as the azo component of the present colorant blends.

The diazo component is preferably a diazotizable aromatic amine sulfonic or carboxylic acid, for example, an amino-substituted benzene, toluene or naphthalene which is also substituted by a water-solubilizing group, a sulfonic acid group, a carboxylic acid group, or a salt form thereof.

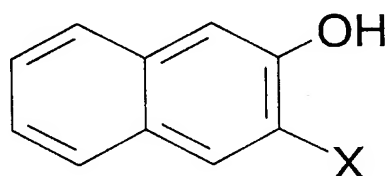
In general, the water-solubilizing substituent is any group capable of forming a water-soluble salt. In particular, the water-solubilizing substituent is an acidic substituent, such as the carboxylic acid or sulfonic acid group mentioned above, or a salt form thereof, in

- 2 -

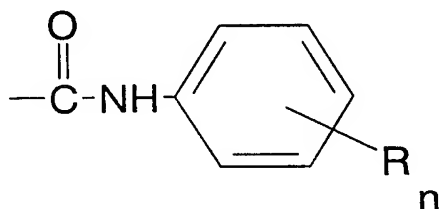
particular, a water-solubilizing salt form, especially an alkali metal salt, such as a sodium or potassium salt.

In general, suitable coupling components are activated aromatic compounds or compounds that contain an activated methylene group which compounds are capable of coupling with the diazotized aromatic amine, especially

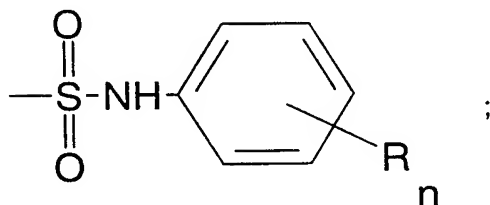
(a) 2-hydroxynaphthalene compounds of the formula



wherein X is H, -COOH, -SO₃H, an amide residue of the formula



or a sulfonamide residue of the formula



wherein R is alkyl, for example methyl or ethyl; alkoxy, for example methoxy or ethoxy; halogen, especially chlorine; nitro; or a 5- or 6- membered heterocycle condensed to the phenyl ring; and wherein n is 0 to 3; and

(b) various pyrazolone derivatives having activated methylene groups, especially 1-phenyl-3-methyl-5-pyrazolone, 1-phenyl-3-carbethoxy-5-pyrazolone or one of their derivatives.

The coupling component may also contain a water-solubilizing substituent.

- 3 -

Preferred coupling components are those described under (a).

Both the diazo and coupling components are unsubstituted or substituted by one or more customary substituents, for example, halogen, especially chlorine; hydroxy and ether derivatives thereof; nitro; alkyl, especially C₁-C₄alkyl, for example, methyl and ethyl; alkoxy, especially C₁-C₄alkoxy, for example, methoxy and ethoxy; -COOH and salts and esters thereof; -SO₃H and salts and esters thereof, carboxamides or sulfonamides, especially N-aryl-substituted carboxamides or sulfonamides, for example N-phenyl-substituted carboxamides or sulfonamides; which customary substituents are unsubstituted or further substituted, especially in the alkyl, alkoxy or aryl groups, by additional customary substituents, for example, trifluoromethyl, which is considered to be a methyl substituent which is further substituted by three fluorines, or 2,4-dichlorophenyl, which is considered to be a phenyl substituent which is further substituted by two chlorines.

Suitable diazo components include 2-amino-4-chloro-5-methylbenzenesulfonic acid, 2-aminonaphthalene-1-sulfonic acid, 2-amino-4-methyl-5-chlorobenzenesulfonic acid, 2-amino-5-methylbenzenesulfonic acid, 2-amino-4-methylbenzenesulfonic acid, 2-methyl-4-aminobenzenesulfonic acid, 2-chloro-5-aminobenzenesulfonic acid, 4-aminobenzenesulfonic acid and 2-amino-4-ethyl-5-chlorobenzenesulfonic acid.

Suitable coupling components include 2-naphthol, 3-hydroxy-2-naphthoic acid, 2-hydroxy-3-naphthanilide, including 2-hydroxy-3-naphth-2'-methylanilide, 2-hydroxy-3-naphth-2'-methoxyanilide, 2-hydroxy-3-naphth-2'-ethoxyanilide, 2-hydroxy-3-naphth-3'-nitroanilide, 2-hydroxy-3-naphth-4'-chloroanilide, 2-hydroxy-3-naphth-4'-methoxyanilide, 2-hydroxy-3-naphth-4'-ethoxyanilide, 2-hydroxy-3-naphth-2',4'-dimethylanilide, 2-hydroxy-3-naphth-2'-methyl-5'-chloroanilide, 2-hydroxy-3-naphth-2'-methoxy-5'-chloroanilide, 2-hydroxy-3-naphth-2',5'-dimethoxyanilide, 2-hydroxy-3-naphth-2',4'-dimethoxy-5'-chloroanilide, 2-hydroxy-3-naphth-2',5'-dimethoxy-4'-chloroanilide, and the corresponding 2-hydroxy-3-naphthsulfonanilides.

Suitable salts of the salt-forming azo components include all metal and ammonium salts. Especially suitable metal salts include alkali metal salts, alkaline earth metal salts, and transition metal salts, such as Mn. The calcium, barium, and strontium salts of the azo

- 4 -

components are especially suitable salts. In general, the salt is chosen such that the azo component is insoluble in the medium that it will be incorporated into.

In particular, azo pigments suitable as the azo component of the present colorant blends include those classified as azo pigment lakes by those skilled in the art, in particular red or orange azo pigment lakes. Specific pigments that are useful as the azo component include the C.I. Pigment Reds and the C.I. Pigment Oranges, including P.R.48, P.R.48:1, P.R.48:2, P.R.48:3, P.R.48:4, P.R.48:5, P.R.49, P.R.49:1, P.R.49:2, P.R.49:3, P.R.50:1, P.R.51, P.R.52:1, P.R.52:2, P.R.53, P.R.53:1, P.R.53:3, P.R.57:1, P.R.58:2, P.R.58:4, P.R.60:1, P.R.63:1, P.R.63:2, P.R.64, P.R.64:1, P.R.66, P.R.67, P.R.68, P.R.151, P.R.200, P.R.237, P.R.239, P.R.240, P.R.243, P.R.247, P.R.247:1; P.O.17, P.O.17:1, P.O.19 and P.O.46; wherein the number indicates the Colour Index designation by which the azo component is commonly known.

Particularly useful azo components include salts of the pigments prepared by the diazo coupling of (A) 2-amino-4-chloro-5-methylbenzenesulfonic acid with 3-hydroxy-2-naphthoic acid (C.I. Pigment Red48), (B) 2-aminonaphthalene-1-sulfonic acid with 2-naphthol (C.I. Pigment Red49), (C) 2-amino-4-methyl-5-chlorobenzenesulfonic acid with 3-hydroxy-2-naphthoic acid (C.I. Pigment Red52), (D) 2-amino-4-methyl-5-chlorobenzenesulfonic acid with 2-naphthol (C.I. Pigment Red53), (E) 2-amino-5-methylbenzenesulfonic acid with 3-hydroxy-2-naphthoic acid (C.I. Pigment Red57), (F) 2-amino-4-ethyl-5-chlorobenzenesulfonic acid with 2-naphthol (C.I. Pigment Orange46). Especially the barium, calcium, manganese, magnesium and strontium salts of these azo compounds.

Particularly useful colorant blends are those wherein the azo component is a red or orange azo pigment lake and the second component is an opaque DPP pigment, including mixtures and solid solutions containing a DPP pigment. If it is desired to maintain the color of the pigment blend upon exposure to light and/or weather, the azo component should have nearly the same hue as the second component.

DPP pigments useful as the second component are well-known in the pigments art and are described, for example, in United States Patent Nos. 4,579,949 and 4,415,685, which are here incorporated by reference. DPP pigments are also known in the pigments art as 3,6-diaryl-1,4-diketopyrrolo[3,4-c]pyrrole pigments and have been described in the chemical

- 5 -

literature as 3,6-diaryl-1,4-diketo-2,5-dihydro-pyrrolo[3,4-c]pyrrole compounds. Preferred DPP components include diphenyl-DPP, di(4-chlorophenyl)-DPP, di(4-tertbutylphenyl)-DPP, di(3-cyanophenyl)-DPP, di(4-cyanophenyl)-DPP, di(biphenyl-4-yl)-DPP and di(4-methylphenyl)-DPP, di(3,4-dichlorophenyl)-DPP.

Opaque solid solution pigments containing a DPP component are also useful as the second component of the present colorant blends. Such solid solution pigments are known in the art and are disclosed, for example, in U.S. Patent Nos. 4,810,304 and 4,783,540, and in U.S. Patent Application Serial Nos. 08/122,025, 08/289,167, 08/314,018, and 08/312,493, which are here incorporated by reference.

According to the present invention, the azo component and second component are combined in any proportions. In general, the weight ratio of the azo component to the second component is from 5:95 to 60:40 in the colorant blends, in particular from 10:90 to 50:50, more specifically from 10:90 to 25:75.

Specific colorant blends that are particularly useful include those colorant blends having an azo component/second component ratio of from 10:90 to 50:50 with the following combinations of azo component/second component: P.R.53:1/unsubstituted DPP; P.R.53:3unsubstituted DPP; P.R.53:1/di(4-chlorophenyl)-DPP; P.R.48:5/di(4-chlorophenyl)-DPP; P.R.48:1/unsubstituted DPP; P.R.48:4/di(biphenyl-4-yl)-DPP; P.R.48:2/di(biphenyl-4-yl)-DPP; P.R.48:3/unsubstituted DPP; P.R.48:5/unsubstituted DPP; P.R.49:1/di(4-chlorophenyl)-DPP; P.R.49:1/di(biphenyl-4-yl)-DPP; P.R.49:2/di(biphenyl-4-yl)-DPP; P.R.49:2/di(4-chlorophenyl)-DPP; P.R.57:1/di(biphenyl-4-yl)-DPP.

The colorant blends of the present invention are characterized by greater than additive lightfastness and weatherfastness than would be expected based on the known properties of the individual components. Thus, ΔE_{blend} is less than ΔE_{calc} for the present colorant blends; wherein ΔE_{blend} is the observed ΔE value of the colorant blend, and ΔE_{calc} is the color difference calculated according to the formula: $\Delta E_{\text{calc}} = (\Delta E_{\text{azo}})(X_{\text{azo}}) + (\Delta E_{\text{sec}})(X_{\text{sec}})$, wherein (ΔE_{azo}) and (ΔE_{sec}) are the observed ΔE values for the azo component and the second component, respectively, and (X_{azo}) and (X_{sec}) are the weight fraction of the azo component and second component, respectively, in the colorant blend.

- 6 -

The hue of the azo component and the second components are preferably as close as possible. In particular, the hue of the second component is preferably within ± 5 units of the hue of the azo component on the CIE Lch scale. Preferably, the hue of the azo component is within ± 3 units of the second component, most preferably within ± 2 units. Such blends show excellent lightfastness and weatherfastness properties.

The CIE Lch system is well-known in the arts relating to colorants, for example the dye and pigments industries. According to the CIE Lch system, every shade is broken down into three measurable components: the L component, which is a measure of lightness, the c component, which is a measure of chroma and the h component which is a measure of hue. Instrumentation for measuring the Lch values is well-known and is commercially available.

Thus, the present invention also relates to a method of selecting pigments to be blended in a colorant blend consisting of an azo component and a second component, which comprises selecting a second component having a hue within 5 units on the CIE Lch scale of the hue of the azo component.

The present invention further relates to a method of preparing a colorant blend which comprises blending an azo component and a second component, wherein the second component has a hue within ± 5 units on the CIE Lch scale of the hue of the azo component. Preferably the hues are within ± 3 units, most preferably within ± 2 units.

Although this invention generally relates to colorant blends wherein the azo and second components have hues within ± 5 units, certain colorant blends with components having a higher hue difference, for example ± 8 or ± 10 units, also have excellent fastness properties wherein ΔE_{blend} is less than 3. For example, colorant blends consisting essentially of Pigment Red 52:2 and di(4-chlorophenyl)-DPP possess excellent fastness properties.

The colorant blends are prepared by methods known in the art for preparing blends of pigment colorants, for example, by simple dry blending and wet blending techniques, preferably by a dry blending technique. For example, the azo component and the second component are blended together by known dry or wet blending techniques and then

- 7 -

dispersed, or, the azo component and the second component are dispersed separately and then the dispersions are blended together into a single dispersion.

The present invention also relates to a method of coloring a high-molecular-weight organic material with a colorant blend described above. Generally, an effective pigmenting amount of the colorant blend is incorporated into the high-molecular-weight organic material to be pigmented, in particular by ball-milling, attritor and other dispersion-milling techniques. An effective pigmenting amount is any amount suitable to provide the desired color in the high-molecular-weight organic material. In particular, the colorant blends are used in an amount of 0.01 to 50% by weight, preferably 1 to 25% by weight, based on the weight of the high-molecular-weight organic material to be pigmented.

The pigmented, high-molecular-weight organic materials which are colored according to the present process are useful in a variety of applications. For example, the high-molecular-weight organic material can be used for the pigmentation of inks, lacquers and enamel coating compositions. The pigmented high-molecular-weight organic materials prepared according to the present invention are particularly useful for preparing automotive coating paints.

The high-molecular-weight organic materials which are colored according to the present process are, for example, cellulose ethers, cellulose esters, polyurethanes, polyesters, polyolefins, polystyrene, polyethers, polyvinyl halides, polytetrafluoroethylene, acrylic and methacrylic polymers, rubber, silicone polymers, phenol/formaldehyde resins, melamine, formaldehyde resins, urea/formaldehyde resins, epoxy resins and diene rubbers or copolymers thereof.

High-molecular-weight organic materials which are useful for heat-curable coatings or cross-linking, chemically-reactive coatings, are also colored according to the present process. Examples of the pigmented, high-molecular-weight organic materials which are used in coatings include acrylic, alkyd, epoxy, phenolic, melamine, urea, polyester, polyurethane, blocked isocyanate, triglycidyl isocyanurate, glycolurils, polyfunctional β -hydroxyalkylamides, benzoguanamine or cellulose ester resins, or combinations thereof. The pigmented, high-molecular-weight organic materials prepared according to the present process are also useful as air-drying or physically-drying coatings, for example,

- 8 -

conventional lacquers such as those used in the cosmetics industry as nail varnishes, for example nitrocellulose lacquers.

The present process is particularly suitable for preparing coatings, for example, industrial coatings and those conventionally employed in the automobile industry, especially in thermosetting systems, such as acrylic/melamine resin, alkyd/melamine resin or thermoplastic acrylic resin systems. The inventive colorant blends are especially suitable for coloring solvent-borne automotive finishes.

The colorant blends are especially suitable for pigmenting the high-molecular-weight organic materials in solid colors, such as masstone colors. However, the colorant blends are also used in effect pigments, such as coated and uncoated micas.

Depending on the end use, it can be advantageous to add specific amounts of texture improving agents to the pigment. Suitable texture improving agents are, in particular, fatty acids of not less than 18 carbon atoms, for example stearic or behenic acid or the amides or metal salts thereof, preferably calcium or magnesium salts, as well as plasticizers, waxes, resin acids such as abietic acid or metal salts thereof, colophonium, alkyl phenols or aliphatic alcohols such as stearyl alcohol or vicinal diols such as dodecane-1,2-diol, and also modified colophonium/- maleate resins or fumaric acid/colophonium resins or polymeric dispersants. The texture improving agents are preferably added in amount of 0.1 to 30%, by weight, most preferably 2 to 15% by weight, based on the final product.

Generally, the inventive colorant blends are suitable for all pigment applications and are distinguished by excellent color strength and opacity, good fastness to light, weathering and heat, excellent purity and saturation, as well as by good dispersability when incorporated into plastics or coatings.

The following examples further illustrate the preferred embodiments of this invention. In these examples, all parts given are by weight unless otherwise noted. All color designations are based on the CIE Lch system.

- 9 -

Example 1: 50 parts of commercially available Pigment Red48:3 (IRGALITE RED 2BSP from CIBA-GEIGY), having a hue component of 30.8, and 50 parts of commercially available di(4-chlorophenyl)-DPP (IRGAZIN RED DPPBO from CIBA-GEIGY), having a hue component of 29.6, the hues being reported in the CIE Lch system, are dry blended in a V-blender to yield a uniform 50:50 blend having a red color with a hue component of 29.7.

Example 2: A masstone panel is prepared from an acrylic-melamine coating based on the following millbase formula:

colorant blend from Example 1	98 parts
acrylic resin	98 parts (69 parts non-volatile)
dispersant	53.6 parts (29.5 parts non-volatile)
solvent	100 parts

The pigmented millbase is dispersed in a temperature-controlled attritor mill for three hours using steel media to yield a millbase dispersion.

A masstone paint is prepared by combining 36.5 parts of the millbase dispersion, 35 parts of acrylic resin, 42 parts alkylated melamine-formaldehyde resin, and 25 parts of a catalyst solution containing dodecylbenzenesulfonic acid as catalyst, N-propylamine and a U.V stabilizer. The masstone paint is then sprayed onto primed aluminum panels and baked for 30 minutes at 250°F. The panels are then exposed to simulated outdoor conditions using a Xenon Arc CI-65 Weather-O-Meter and a schedule similar to ASTM G26-70. Since the ΔE observed for Pigment Red48:3 alone after 2000 hours exposure is 11.5, and the ΔE observed for di(4-chlorophenyl)-DPP alone after 2000 hours exposure is 0.8, the observed ΔE of 1.0 after 2000 hours exposure for the colorant blend of the present invention is much less than would be expected based on the observed ΔE values of the individual components.

Example 3: The procedure of Example 2 is followed with a 35:65 colorant blend containing 35 parts of Pigment Red48:3 and 65 parts di(4-chlorophenyl)-DPP. After 2000 hours exposure, a ΔE of 0.4 is observed.

Example 4: The procedure of Example 2 is followed with a 25:75 colorant blend containing 25 parts of Pigment Red48:3 and 75 parts di(4-chlorophenyl)-DPP. After 2000 hours of exposure a ΔE of 0.8 is observed.

Example 5: The procedure of Example 2 is followed with a 10:90 colorant blend which contains 10 parts of Pigment Red48:3 and 90 parts di(4-chlorophenyl)-DPP. After 2000 hours exposure a ΔE of 1.1 is observed.

Example 6: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red48:2. After 2000 hours exposure, a ΔE of 1.8, 1.6 and 1.4 is observed with the 50:50 blend, the 25:75 blend and the 10:90 blend, respectively.

Example 7: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red48:2 and the di(4-chlorophenyl)-DPP is replaced by di(biphenyl-4-yl)-DPP. After 2000 hours exposure, a ΔE of 1.2, 1.1 and 1.4 is observed for the masstone panels 50:50 blend, the 25:75 blend and the 10:90 blend, respectively.

Example 8: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red52:2 and the di(4-chlorophenyl)-DPP is replaced by di(biphenyl-4-yl)-DPP. After 2000 hours exposure, a ΔE of 0.9, 0.7 and 0.6 is observed for the 50:50 blend, the 25:75 blend and the 10:90 blend, respectively.

Example 9: The procedure of Examples 2 and 4 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red49:2 and the di(4-chlorophenyl)-DPP is replaced by di(biphenyl-4-yl)-DPP. After 2000 hours exposure, a ΔE of 0.3 and 0.4 is observed for the 50:50 blend and the 25:75 blend, respectively.

Example 10: The procedure of Example 4 is followed with a colorant blend wherein the Pigment Red48:3 is replaced with Pigment Red57:1 and the di(4-chlorophenyl)-DPP is replaced by di(biphenyl-4-yl)-DPP. After 2000 hours exposure, a ΔE of 0.7 is observed for the 25:75 blend.

Example 11: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red53:1 and the di(4-chlorophenyl)-DPP is replaced by unsubstituted DPP. After 2000 hours exposure, a ΔE of 1.7, 0.9 and 0.4 is observed for the 50:50 blend, the 25:75 blend and the 10:90 blend, respectively.

Example 12: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with the Sr salt of Pigment Red53 and the di(4-chlorophenyl)-DPP is replaced by unsubstituted DPP. After 2000 hours exposure, a ΔE of 1.6, 1.0 and 0.5 is observed for the 50:50 blend, the 25:75 blend and the 10:90 blend, respectively.

Example 13: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red49:1. After 2000 hours exposure, a ΔE of 1.4, 1.4 and 1.9 is observed for the 50:50 blend, the 25:75 blend and the 10:90 blend, respectively.

Example 14: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red48:1. After 2000 hours exposure, a ΔE of 1.6, 0.4 and 0.8 is observed for the 50:50 blend, the 25:75 blend and the 10:90 blend, respectively.

Example 15: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red48:5 (Mg salt). Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 16: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red53:1. Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 17: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red48:1 and the di(4-chlorophenyl)-

DPP is replaced by unsubstituted DPP. Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 18: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the di(4-chlorophenyl)-DPP is replaced by unsubstituted DPP. Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 19: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red48:5 and the di(4-chlorophenyl)-DPP is replaced by unsubstituted DPP. Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 20: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Orange19 and the di(4-chlorophenyl)-DPP is replaced by di(4-tert-butylphenyl)-DPP. Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 21: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Orange46 and the di(4-chlorophenyl)-DPP is replaced by opaque di(3-cyanophenyl)-DPP. Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 22: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red48:4 and the di(4-chlorophenyl)-DPP is replaced by di(biphenyl-4-yl)-DPP. Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 23: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the di(4-chlorophenyl)-DPP is replaced by an opaque red solid solution consisting of 40 parts of unsubstituted DPP and 60 parts of di(4-chlorophenyl)-DPP. Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 24: Example 27 is repeated except that the Pigment Red 48:3 is replaced by the following azo components: P.R.48:5 and P.R.53:1. In each instance, a colorant blend which shows very good lightfastness and weatherfastness is obtained.

Example 25: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the P.R.48:3 is replaced with P.R.48:1 and the di(4-chlorophenyl)-DPP is replaced by an opaque red solid solution consisting of 32 parts unsubstituted DPP, 48 parts di(4-chlorophenyl)DPP and 20 parts 2,9-dichloroquinacridone. Colorant blends with very good lightfastness and weatherfastness are obtained.

Example 26: The procedure of Example 29 is repeated except that the Pigment Red48:3 is replaced by the following azo components: P.R.48:5 and P.R.53:1. In each instance, a colorant blend which shows very good lightfastness and weatherfastness is obtained.

Example 27: The procedure of Examples 2, 4 and 5 are followed with colorant blends wherein the Pigment Red48:3 is replaced with Pigment Red48:4. After 2000 hours exposure, a ΔE of 1.9, 1.1, and 0.2 is observed for the 50:50 blend, the 25:75 blend and the 10:90 blend, respectively.

Example 28: 50:50 tints are prepared by standard procedures with TiO_2 and the colorant blends used in Examples 4 and 5. After 2000 hours of exposure, a ΔE of 3.4 and 2.1 is observed for the 25:75 and 10:90 blends, respectively.

Example 29: A 50:50 tint with the 10:90 colorant blend of Example 27 and TiO_2 is prepared by standard procedures. After 2000 hours of exposure, a ΔE of 1.5 is observed.

Example 30: A 50:50 tint with the 25:75 colorant blend of Example 27 and TiO_2 is prepared by standard procedures. After 2000 hours of exposure, a ΔE of 2.8 is observed.

Example 31:

Millbase A - 100 parts of a millbase is prepared by combining 28 parts of di(4-chlorophenyl)-DPP, 19 parts of acrylic resin, 9 parts of dispersant and 44 parts of xylene.

Millbase B - 100 parts of a millbase is prepared by combining 16 parts of Pigment Red 48:3, 27 parts of acrylic resin, 5 parts of dispersant and 52 parts of xylene.

Masstone Paints

I. 137.3 parts of a masstone paint containing 10 parts of Pigment Red48:3 and 90 parts of di(4-chlorophenyl)-DPP is prepared by combining 36.6 parts of millbase A, 7.1 parts of millbase B, 37.4 parts of acrylic resin (68% solids), 28.1 parts of alkylated melamine-formaldehyde resin and 28.1 parts of a catalyst/stabilizer solution. Weatherometer testing yields results similar to those obtained in Example5.

II. 137.6 parts of a masstone paint containing 25 parts of Pigment Red48:3 and 75 parts of di(4-chlorophenyl)-DPP is prepared by combining 30.1 parts of millbase A, 17.5 parts of millbase B, 34.5 parts of acrylic resin, 27.7 parts of alkylated melamine-formaldehyde resin and 27.8 parts of a catalyst/stabilizer solution. Weatherometer testing yields results similar to those obtained in Example4.

III. 137.9 parts of a masstone paint containing 50 parts of Pigment Red48:3 and 50 parts of di(4-chlorophenyl)-DPP is prepared by combining 19.6 parts of millbase A, 34.3 parts of millbase B, 29.8 parts of acrylic resin, 27.1 parts of alkylated melamine-formaldehyde resin and 27.1 parts of a catalyst/stabilizer solution. Weatherometer testing yields results similar to those obtained in Example2.

Example 32: Solvent-based mica paint formulation

Mica Base

746 parts of a mica base is prepared by mixing 251 parts of pearlescent mica with 251 parts of acrylic resin and 244 parts of butyl acetate until lump free.

Mica Paint Formulation

A mica basecoat paint formulation is prepared by mixing 128 parts of the pigmented millbase dispersion prepared in Example2, 70 parts of the mica base, 20.8 parts of a nonaqueous dispersion resin, 30.6 parts of melamine resin, 2.6 parts of UV screener and 3.5 parts of catalyst. The final mica basecoat paint is prepared by diluting with xylene to a spray viscosity of about 20 seconds with a #4 Ford Cup.

- 15 -

The mica basecoat paint is sprayed onto aluminum panels. After a flash period of about 3 minutes, an acrylic-melamine clear topcoat is applied on top of the color basecoat. The panels are then allowed to flash for 10 minutes and then baked for 30 minutes at 130°C.

The coating possesses attractive color with very good lightfastness and weatherfastness properties. Similar attractive panels are obtained using the colorant blends of Examples 3-27 in place of the pigment of Example 1 in the pigmented millbase dispersion.

Example 33: A powder coating is prepared by pre-blending 8 parts of the colorant blend of Example 1 with 84 parts of polyester resin, 6.4 parts of a triglycidyl isocyanurate cross-linking agent, 1 part of flow control agent and 0.5 parts of benzoin. The pre-blended mixture is then fed into a twin screw extruder. The extrudate is cooled, ground and sieved through a 120 mesh screen to yield the powder coating.

The powder coating is sprayed onto aluminum panels by standard methods and then cured at 200°C for 15 minutes. The coating possesses attractive color with very good lightfastness and weatherfastness properties. Similar attractive panels are obtained using the colorant blends of Examples 3-27 in place of the pigment of Example 1.

Example 34: A pigmented, flexible polyvinyl chloride sheet is prepared by standard techniques from a mixture containing 1 part of the colorant blend of Example 1, 100 parts of PVC resin, 100 parts of plasticizer, 18 parts of calcium carbonate and 3 parts of stabilizer. The resulting flexible PVC sheet shows very little specking or streaking. Similar PVC sheets are obtained when the colorant blends of Examples 3-27 replace the colorant blend of Example 1.

WE CLAIM:

1. A colorant blend, which contains (a) an azo component, which azo component is a salt of a salt-forming azo pigment of the formula

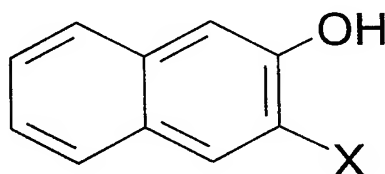


wherein A is the residue of a diazo component and B is the residue of a coupling component; and (b) a second component, which second component is an opaque DPP pigment having a hue within ± 5 units of the azo component.

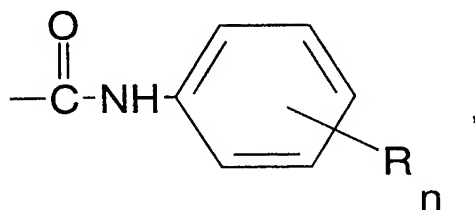
2. A colorant blend of claim 1 wherein the diazo component is a diazotizable amine containing an acidic substituent, such as a sulfonic or carboxylic acid substituent, or a salt form thereof, in particular an alkali metal salt, such as a sodium or potassium salt.

3. A colorant blend of claim 2 wherein the diazo component is an amino-substituted benzene, toluene or naphthalene which is further substituted by a water-solubilizing group, a sulfonic acid group, a carboxylic acid group, or a salt form thereof.

4. A colorant blend of claim 3 wherein the coupling component is a 2-hydroxynaphthalene compound of the formula

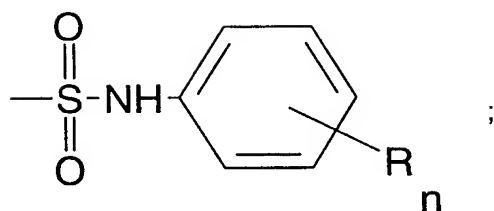


wherein X is H, -COOH, -SO₃H, an amide residue of the formula



or a sulfonamide residue of the formula

- 17 -



wherein R is alkyl, for example methyl or ethyl; alkoxy, for example methoxy or ethoxy; halogen, especially chlorine; nitro; or a 5- or 6- membered heterocycle condensed to the phenyl ring; and wherein n is 0 to 3.

5. A colorant blend of claim 1 wherein the diazo and coupling components are unsubstituted or substituted by one or more customary substituents; which substituents may be further substituted, especially in the alkyl, alkoxy or aryl groups, by additional customary substituents.

6. A colorant blend of claim 1 wherein the diazo component is 2-amino-4-chloro-5-methylbenzenesulfonic acid, 2-aminonaphthalene-1-sulfonic acid, 2-amino-4-methyl-5-chlorobenzenesulfonic acid, 2-amino-5-methylbenzenesulfonic acid, 2-amino-4-methylbenzenesulfonic acid, 2-methyl-4-aminobenzenesulfonic acid, 2-chloro-5-aminobenzenesulfonic acid, 4-aminobenzenesulfonic acid or 2-amino-4-ethyl-5-chlorobenzenesulfonic acid.

7. A colorant blend of claim 1 wherein the coupling component is 2-naphthol, 3-hydroxy-2-naphthoic acid, a 2-hydroxy-3-naphthanilide, including 2-hydroxy-3-naphth-2'-methylanilide, 2-hydroxy-3-naphth-2'-methoxyanilide, 2-hydroxy-3-naphth-2'-ethoxyanilide, 2-hydroxy-3-naphth-3'-nitroanilide, 2-hydroxy-3-naphth-4'-chloroanilide, 2-hydroxy-3-naphth-4'-methoxyanilide, 2-hydroxy-3-naphth-4'-ethoxyanilide, 2-hydroxy-3-naphth-2',4'-dimethylanilide, 2-hydroxy-3-naphth-2'-methyl-5'-chloroanilide, 2-hydroxy-3-naphth-2'-methoxy-5'-chloroanilide, 2-hydroxy-3-naphth-2',5'-dimethoxyanilide, 2-hydroxy-3-naphth-2',4'-dimethoxy-5'-chloroanilide, 2-hydroxy-3-naphth-2',5'-dimethoxy-4'-chloroanilide, and the corresponding 2-hydroxy-3-naphthsulfonanilides.

8. A colorant blend of claim 7 wherein the diazo component is 2-amino-4-chloro-5-methylbenzenesulfonic acid, 2-aminonaphthalene-1-sulfonic acid, 2-amino-4-methyl-5-chloro-

- 18 -

benzenesulfonic acid, 2-amino-5-methylbenzenesulfonic acid, 2-amino-4-methylbenzenesulfonic acid, 2-methyl-4-aminobenzenesulfonic acid, 2-chloro-5-aminobenzenesulfonic acid, 4-aminobenzenesulfonic acid or 2-amino-4-ethyl-5-chlorobenzenesulfonic acid.

9. A colorant blend of claim 1 wherein the azo component is an alkali metal, alkaline earth metal, a transition metal, calcium, barium, or strontium salt.

10. A colorant blend of claim 1 wherein the azo component is selected from among the C.I. Pigment Reds and C.I. Pigment Oranges, including P.R.48, P.R.48:1, P.R.48:2, P.R.48:3, P.R.48:4, P.R.48:5, P.R.49, P.R.49:1, P.R.49:2, P.R.49:3, P.R.50:1, P.R.51, P.R.52:1, P.R.52:2, P.R.53, P.R.53:1, P.R.53:3, P.R.57:1, P.R.58:2, P.R.58:4, P.R.60:1, P.R.63:1, P.R.63:2, P.R.64, P.R.64:1, P.R.66, P.R.67, P.R.68, P.R.151, P.R.200, P.R.237, P.R.239, P.R.240, P.R.243, P.R.247, P.R.247:1; P.O.17, P.O.17:1, P.O.19 and P.O.46.

11. A colorant blend of claim 1 wherein the second component is a DPP pigment or a solid solution containing a DPP pigment.

12. A colorant blend which contains Pigment Red 52:2 and di(4-chlorophenyl)-DPP.

13. A colorant blend of claim 11 wherein the DPP component is compound selected from the group consisting of diphenyl-DPP, di(4-chlorophenyl)-DPP, di(4-tertbutylphenyl)-DPP, di(3-cyanophenyl)-DPP, di(4-cyanophenyl)-DPP, di(biphenyl-4-yl)-DPP and di(4-methylphenyl)-DPP, di(3,4-dichlorophenyl)-DPP; including solid solutions containing the above-identified compounds.

14. A colorant blend of claim 1 wherein the weight ratio of the azo component to the second component is from 5:95 to 60:40, in particular from 10:90 to 50:50, more specifically from 10:90 to 25:75.

15. A colorant blend of claim 1 wherein the hue of the second component is within ± 3 units of the hue of the azo component.

- 19 -

16. A method of selecting pigments to be blended in a colorant blend consisting of an azo component and a second component, which comprises selecting a second component having a hue within 5units of the hue of the azo component.

17. A method of preparing a colorant blend according to claim 1, which comprises blending an azo component and a second component, wherein the second component has a hue within ± 5 units, preferably within ± 3 units, most preferably within ± 2 units, of the hue of the azo component.

18. A method of preparing a colorant blend of claim 1, wherein the azo component and the second component are blended together by known dry or wet blending techniques and then dispersed, or, the azo component and the second component are dispersed separately and then the dispersions are blended together into a single dispersion.

19. A method of coloring a high-molecular-weight organic material with a colorant blend, which comprises incorporating a colorant blend of claim 1 into the high-molecular-weight organic material.

20. A method of claim 18, wherein the high-molecular-weight organic material is an automotive paint.

21. A colorant blend of claim 1 wherein the azo component/second component ratio is from 10:90 to 50:50 with the following combinations of azo component/second component:
P.R.53:1/unsubstituted DPP; P.R.53:3/unsubstituted DPP; P.R.53:1/di(4-chlorophenyl)-DPP; P.R.48:5/di(4-chlorophenyl)-DPP; P.R.48:1/unsubstituted DPP; P.R.48:4/di(biphenyl-4-yl)-DPP; P.R.48:2/di(biphenyl-4-yl)-DPP; P.R.48:3/unsubstituted DPP;
P.R.48:5/unsubstituted DPP; P.R.49:1/di(4-chlorophenyl)-DPP; P.R.49:1/di(biphenyl-4-yl)-DPP; P.R.49:2/di(biphenyl-4-yl)-DPP; P.R.49:2/di(4-chlorophenyl)-DPP;
P.R.57:1/di(biphenyl-4-yl)-DPP.

22. A colorant blend of claim 1 wherein the coupling component is a pyrazolone derivative having an activated methylene group, especially 1-phenyl-3-methyl-5-pyrazolone, 1-phenyl-3-carbethoxy-5-pyrazolone or one of their derivatives.

- 20 -

23. A colorant blend of claim 1 wherein the azo component is a monoazo or disazo pigment.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/02991

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09B67/22 C09B63/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2 508 448 A (A.A. BRIZZOLARA) 23 May 1950 see column 2, line 43 - column 3, line 44; examples ---	1-23
Y	EP 0 224 445 A (CIBA GEIGY AG) 3 June 1987 see the whole document ---	1-23
A	EP 0 535 774 A (TOYO INK MFG CO) 7 April 1993 see abstract --- -/--	1-23

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
 "&" document member of the same patent family

Date of the actual completion of the international search

4 February 1998

Date of mailing of the international search report

18/02/1998

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Dauksch, H

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/02991

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 8413 Derwent Publications Ltd., London, GB; Class E21, AN 84-078792 XP002054561 & JP 59 030 862 A (TOYO INK MFG CO) , 18 February 1984 see abstract</p> <p style="text-align: center;">---</p>	1-23
A	<p>EP 0 243 304 A (CIBA GEIGY AG) 28 October 1987 see abstract; examples 3,4</p> <p style="text-align: center;">---</p>	1-23
A	<p>EP 0 277 914 A (CIBA GEIGY AG) 10 August 1988 see abstract & US 4 810 304 A cited in the application</p> <p style="text-align: center;">-----</p>	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/02991

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2508448 A	23-05-50	NONE	
EP 0224445 A	03-06-87	CA 1289964 A DE 3681261 A JP 2572555 B JP 7173406 A JP 2551565 B JP 62149759 A US 4914211 A US 4791204 A	01-10-91 10-10-91 16-01-97 11-07-95 06-11-96 03-07-87 03-04-90 13-12-88
EP 0535774 A	07-04-93	JP 5098200 A DE 69204411 D DE 69204411 T	20-04-93 05-10-95 01-02-96
EP 0243304 A	28-10-87	CA 1309207 A DE 3786038 A DE 3786038 T JP 2109926 C JP 8016200 B JP 62295966 A US 4844742 A	20-10-92 08-07-93 14-10-93 21-11-96 21-02-96 23-12-87 04-07-89
EP 0277914 A	10-08-88	DE 3851346 D ES 2058327 T JP 2573642 B JP 63201189 A KR 9602229 B US 4810304 A	13-10-94 01-11-94 22-01-97 19-08-88 13-02-96 07-03-89